

OXIDATION PROTECTION OF NIOBIUM BY A  $\text{NbSi}_2$  LAYER,  
IMPREGNATED WITH  $\text{SnAl}$ 

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Protective oxidation-resistant coatings on pure niobium, as used in aircraft parts, by a  $\text{NbSi}_2$  layer impregnated with  $\text{SnAl}$  are described on hand of several diagrams and photomicrographs. The protective effect of the "cladding" is primarily due to the tin-aluminum phase, rich in tin, distributed within the silicide, which acts as a barrier for the oxygen by forming an  $\text{Al}_2\text{O}_3$  film at the surface of the coating. Manufacture of the coating, by reaction with niobium in a tin-aluminum-silicon bath, is described. The highly mobile phase incorporated in a porous matrix, which latter acts as carrier for the liquid phase, forms a barrier for diffusion of the liquid phase and permits self-healing of minor surface flaws.

A. Introduction

The use of alloys, resistant to elevated temperatures, often is closely linked to the problem of oxidation protection at high temperatures.

In view of its specific properties, niobium is of considerable interest as a base for heat-resistant alloys.

However, niobium has only a minimal resistance to oxidation. This drawback is shared by niobium with other refractory metals.

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\* Numbers in the margin indicate pagination in the original foreign text.

Consequently, the use of niobium or niobium alloys in an oxidizing atmosphere is impossible without the use of protective surface coatings. Depending on the end use, a given coating must meet a certain number of different requirements. It is hardly possible to obtain all of the desired properties on the basis of simple technical and metallurgical concepts.

Among the properties required of a coating system, the three shown in /2 our first slide are of a fundamental nature:

- 1) High oxidation resistance of the protective coating and total suppression of any oxygen diffusion in the base metal.
- 2) Compatibility of protective coating and base metal. Their properties must under no circumstances be negatively influenced by an interaction due to diffusion.
- 3) Self-healing features of the coating, which will permit a certain tolerance of flaws.

The first two points determine the chemical composition of the coating. For niobium and its alloys, protective coatings on a silicon or aluminum base were found especially suitable until now.

With respect to the property of so-called self-healing, this is necessary for ensuring protection in practical use. In fact, it is practically impossible on the one hand, to produce coatings with 100% absence of flaws; on the other hand, to avoid the formation of hair cracks or other defects in practical use.

These considerations also apply to coatings on a base of intermetallic phases. Coatings of such type produce satisfactory adherence since they grow by reaction between a metal and another element and thus form a permanent composite. However, their ductility is low. In most cases, a total adaptation of the ex-

pansion properties of the coating to those of the base metal is impossible. Consequently, formation of cracks and other defects in the layer, produced by temperature fluctuations, must be expected.

Thus, self-healing properties are indispensable so as to avoid a catastrophic oxidation. Self-healing presupposes that the coating contains mobile phases. Several examples for a partial practical application of this concept are in existence, as shown in our next slide (No.2).

Satisfactory self-healing properties were obtained, for example, in zinc <sup>/3</sup> coatings with embedded niobium. In this case, the high zinc vapor tension of the niobium-zinc phases is responsible for these excellent properties. However, this very same phenomenon also limits the practical possibilities of using this coating at temperatures below 1100°C.

Protective coatings of molybdenum silicide also exhibit a certain self-healing capability at elevated temperatures. This can be attributed to the formation of a vitreous surface film of SiO<sub>2</sub>.

Self-healing properties were also encountered in coatings which, in addition to the intermetallic phase, enclose a liquid phase. The following examples are typical:

liquid gold-silicon, incorporated into a porous MoSi<sub>2</sub> phase enclosing molybdenum;

tin-aluminum and tantalum aluminide, enclosing tantalum;

Al<sub>2</sub>O<sub>3</sub> impregnated by silicate-base glass, enclosing niobium.

#### B. Structure and Mode of Action of the NbSi<sub>2</sub>/SnAl Coating

The coating system to be discussed here is based on the same principle. Our next slide (No.3) shows a coating of this type after manufacture. In

principle, the coating is composed of a porous matrix into which a liquid phase is incorporated. The matrix consists of an intermetallic compound; in our case, the compound is  $\text{NbSi}_2$ . The liquid phase enclosed in the matrix is tin-aluminum.

The structural principle on which this coating system is based seems generally suitable for coatings to be used at high temperatures. It offers the advantage of utilizing the excellent protective properties of a liquid phase, since this phase has high mobility and a satisfactory resistance to oxidation. The porous intermetallic phase has three different functions:

carrying the liquid phase;

/4

preventing diffusion of the liquid phase in the base material;

having a certain resistance to oxidation.

The composition of the two phases can be varied, which permits an adaptation of the coating to the desired end use, in each specific case.

The next slide (No.4) shows the layer during oxidation. The protective effect is primarily produced by the tin-aluminum phase, distributed in the silicide. This phase acts as a barrier for the oxygen, by forming an  $\text{Al}_2\text{O}_3$  film at the surface of the coating.

### C. Production of the Coating

Such a coating can be produced by reacting niobium in a tin-aluminum-silicon bath. The next slide (No.5) shows the various manufacturing stages. The following stages can be differentiated:

taking specimens;

preparing the surface;

producing the coating by diffusion treatment;

cleaning the specimens to eliminate the excess tin-aluminum.

The most important parameters to be checked are as follows:

- surface condition of the specimen;
- radius of the ridges;
- duration and temperature of treatment;
- composition of the bath.

The next slide (No.6) shows the first stage of formation of  $\text{NbSi}_2$ . If the parameters are carefully selected, dendritic  $\text{NbSi}_2$  crystals will form, with the tin-aluminum phase located between these dendrites. The optimum thickness of the coatings varies from 100 to 200  $\mu$ .

The refining of a protective coating requires thorough knowledge of the 15 phenomena produced within the layer during oxidation. The following points are of specific importance here:

- Behavior of each individual component; particularly behavior toward oxidation.

- Diffusion-induced interaction of the constituents of the coating and of the base metal.

- Determination of the causes for the loss of protective effect of the coating, after a certain oxidation time.

For this reason, we first made separate studies of the behavior of the liquid component and that of the matrix.

#### D. Oxidation Behavior of the Two Phases

##### 1. Tin-Aluminum Phase

The oxidation behavior of the tin-aluminum phase was investigated in air of different temperatures. The next slide (No.7) shows the changes in weight, observed during an oxidation at 1100°C.

If the tin-aluminum alloy has an aluminum content above 5%, it will form a highly stable oxide layer. The formation of such an oxide layer preserves the initial shape of the solid material, even at temperatures above the fusion point. For example, specimens in the form of rods can be observed in the liquid state.

## 2. NbSi<sub>2</sub> Phase

The oxidation behavior of the NbSi<sub>2</sub> phase is demonstrated in our next slide (No.8). The NbSi<sub>2</sub> phase has a moderate oxidation resistance at temperatures above 1000°C. Alloying additions such as, for example, titanium or others may further decrease the oxidation rate. Considerable influence is also exerted by the stoichiometric composition. This particular slide shows that the oxidation rate of NbSi<sub>2</sub>, with an excess of silicon, is much slower than that of NbSi<sub>2</sub>, with an excess of niobium. Probably, the silicide is protected from extremely 6 rapid oxidation by the formation of vitreous SiO<sub>2</sub> films.

At temperatures between 600° and 900°C, the NbSi<sub>2</sub> - as other silicides - exhibits the phenomenon known as "pest". Our next slide (No.9) shows this phenomenon. The process consists in a rapid oxidation in the temperature domain in question, followed by desaggregation into powder of an intermetallic phase. At higher temperatures, this phase exhibits a satisfactory oxidation resistance. The "pest" can be avoided by certain alloying additions, such as titanium, as indicated in this particular slide.

The influence exerted by titanium is demonstrated by the next slide (No.10) which shows curves of the oxidation rate at various temperatures. To determine the susceptibility to "pest", the specimens were heated to 1200°C in steps of 300°C/hr, and then cooled at the same rate. As indicated by this diagram, pure

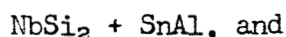
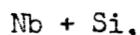


$\text{NbSi}_2$  shows destructive oxidation on cooling, near  $1000^\circ\text{C}$ . The oxidation behavior is basically changed by the addition of titanium. Accelerated oxidation is already suppressed by an addition of 10 at.% titanium. This percentage refers to the niobium content. The phenomenon of "pest" can thus be controlled by additions of titanium or other elements.

#### E. Structural Modifications of the Layer at Elevated Temperatures

After having demonstrated the behavior of each of the two constituents of the coating, we will now describe their interaction within the coating aggregate. After production of the coating, the individual components will be in thermo- 7 dynamic disequilibrium. This means that, at elevated temperatures, modifications will take place in the coating system. Such modifications are basically produced by two phenomena: diffusion and oxidation.

The possible modifications of the layer, due to diffusion, are schematically sketched in the next slide (No.11). Three reactions can be differentiated, namely,



recrystallization of  $\text{NbSi}_2$ .

The reactions between niobium and silicon as well as the recrystallization of  $\text{NbSi}_2$  are the most important with respect to the lifetime of the specimens.

The next slide (No.12) shows the effect of the reaction between niobium and silicon. Two interface layers are formed by the reaction between  $\text{NbSi}_2$  and niobium, due to diffusion. These are two silicides richer in niobium than  $\text{NbSi}_2$ . Their growth is much more rapid at  $1400^\circ$  than at  $1100^\circ\text{C}$ .

Another slide (No.13) shows the modifications produced by the recrystalliza-

tion of  $\text{NbSi}_2$ . Due to the temperature effect, the grains of  $\text{NbSi}_2$  begin to coarsen. It is highly probable that the interaction between the tin-aluminum and  $\text{NbSi}_2$  phases exerts a great influence on the reaction kinetics. It can be seen that, after a certain time, the structure is strongly modified and that, after a still longer time, the liquid tin-aluminum phase will agglomerate in a few very large interstices.

As demonstrated in the next slide (No.14), oxidation of the layer constitutes a chemical reaction that leads to a depletion of the tin-aluminum and  $\text{NbSi}_2$  phases. This chemical reaction converts the metallic phases into oxide phases. The velocity of these reactions is also determined by the diffusion. The metallic ions must traverse the formed oxide layers to become converted, in turn, into oxide which is deposited at the interface. /8

The depletion of the coating by oxidation, on the one hand, and the structural changes due to diffusion, on the other hand, are the cause of failure of the coating.

The next slide (No.15) illustrates the combined effect of these two influences. The modifications suffered by the layer during an oxidation can be described as follows:

At the beginning of oxidation, the  $\text{Al}_2\text{O}_3$  film ensures the protective effect on the surface of the coating.

After a certain time, formation of an intermediary layer between the  $\text{NbSi}_2$  phase and the niobium will start. Actually, a new phase of silicide is formed, namely,  $\text{Nb}_5\text{Si}_3$ . In addition, the recrystallization of the niobium silicide causes a modification of its structure. This, in turn, leads to a change in the distribution of the liquid phase within the coating. This results in an agglomeration of droplets which originally had been finely divided.

If this agglomeration and the recrystallization of  $\text{NbSi}_2$  progress further, giant crystals will form. At this stage, the aluminum oxide layer becomes defective and a layer of  $\text{SiO}_2$  now takes over in part the role of protection. Coatings whose matrix is composed of pure  $\text{NbSi}_2$ , i.e., without other alloying addition, exhibit susceptibility to the "pest" at this stage.

The true cause of failure of the coating depends on the velocity at which these phenomena proceed. In most of the cases, failure is due to structural changes of the coating produced by diffusion. The depletion of the phases by oxidation is not generally the cause of failure of the protective coating.

#### F. Lifetime

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Finally, we will give a few examples for the lifetime of a certain number of coated specimens. The next slide (No.16) shows the values obtained by us. The diagram indicates the percentage of specimens that have attained a given lifetime at a certain temperature.

Our results relate to the following conditions:

The oxidation tests were made at constant temperatures.

The "lifetime" denotes the time elapsed until appearance of the first visible sign of change on the surface of the specimen.

The oxidation atmosphere consisted of static air, in electrically heated furnaces.

The next slide (No.17) compares the values obtained by us with the mean values recently published in the literature. However, one reservation should be made here: Strict comparisons are impossible, since the experimental conditions had not been standardized. The curve of the maximum values indicates the results one can hope to obtain with the coating developed by us on a base of

pure niobium. It is obvious that this curve exceeds the upper limit of the values given in the literature, specifically at low temperature.

All our results, shown in this diagram, refer to specimens of pure unalloyed niobium. As already explained, such specimens become susceptible to the "pest" after a certain time. For this reason, they will fail at excessive temperature variations. If a satisfactory resistance to temperature fluctuations is desired, the niobium must be alloyed. The following slide (No.18) demonstrates the difference between the specimens of pure niobium and a niobium-titanium alloy. The photographs show two specimens which had been subjected to 120 heating and cooling cycles between 150° and 1200°C. Each cycle lasted twice 15 min. It is quite obvious that the protective effect is greater in the case of the specimen with a certain content of titanium.

#### G. Summary

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In conclusion, the structure of the coating in question can be summarily described as follows:

A highly mobile phase is incorporated into a porous matrix. The matrix has several functions:

Acting as a carrier of the liquid phase.

Constituting a barrier for the diffusion of the liquid phase.

Possibly acting as a barrier for oxidation.

The porous phase, combined with a liquid phase, permits self-healing of minor surface flaws, such as crazings that might be produced during manufacture of the coating or during its practical use.

The configuration of the described coating permits its adaptation to other systems. The last slide (No.19) gives an example of such an adaptation for a

molybdenum screw.

In conclusion, it should be mentioned that basic research must accompany and run parallel to the development of a given coating. Knowledge of the behavior of the various components at elevated temperatures is indispensable, which is true also of their interaction. The resultant data will then permit conclusions as to the causes of failure of the coating and make improvement of the latter possible.

The described investigations were conducted at the Battelle Institute at Geneva, within the research project for the D.R.M.E.

#### LIST OF SLIDES

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- No.2 - Examples of Coating Systems
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- No.4 - Structure of the Layer during Oxidation
- No.5 - Production of the Specimens
- No.6 - Formation of the Porous  $\text{NbSi}_2/\text{SnAl}$  Layer
- No.7 - Change in Weight of the  $\text{SnAl}$  Specimens during Oxidation at  $1100^\circ\text{C}$
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- |   |   |                                  |
|---|---|----------------------------------|
| 1) High oxidation resistance                | } | Determined by:                   |
| 2) Compatibility of coating with base metal |   | chemical composition             |
| 3) Self-healing                             | } | mobility of the protective phase |

Fig.1 Qualities Required of the Coating

	Without Liquid Phase		With Liquid Phase		
Base metal	Nb	Mo	Mo	Ta	Nb
Coating					
Intermetallic phase	Nb-Zn	MoSi <sub>2</sub>	MoSi <sub>2</sub>	Nb-Al	Nb <sub>2</sub> O <sub>5</sub>
Liquid phase	—	—	Si	—	—
Mobile phase	Zn	SiO <sub>2</sub>	Si	—	—
Type	metal	oxide	metal	metal	oxide

Fig.2 Examples of Coating Systems

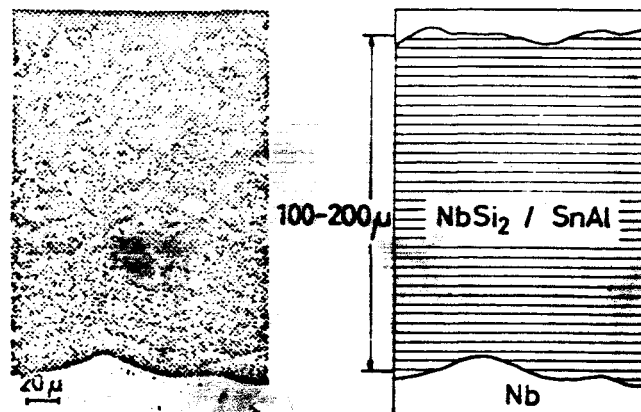


Fig.3 Structure of the Layer after Manufacture

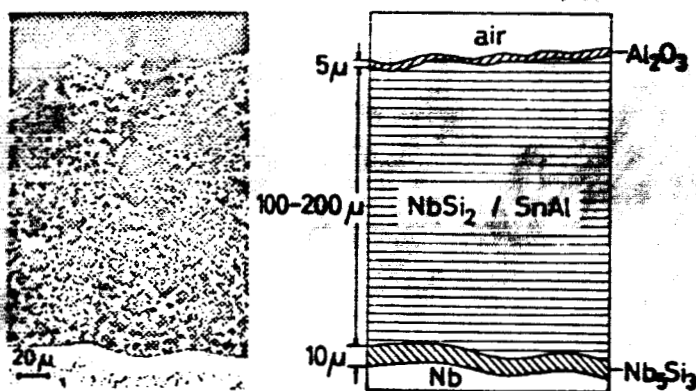
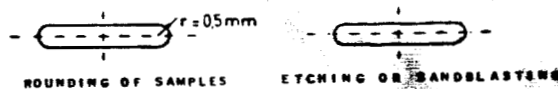


Fig.4 Structure of the Layer during Oxidation

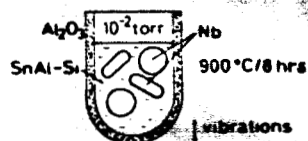
## I) Taking the Specimens



## II) Preparation of the Surface



## III) Treatment by diffusion



## IV) Elimination of Excess of SnAl

Finished Sample



Fig.5 Production of the Specimens



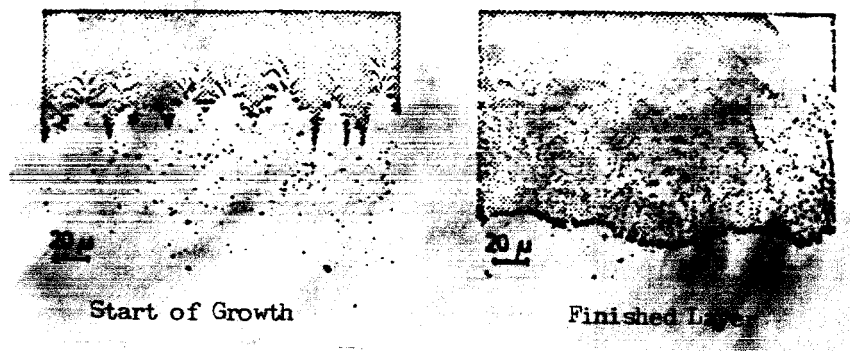


Fig.6 Formation of the Porous  $\text{NbSi}_2/\text{SnAl}$  Layer

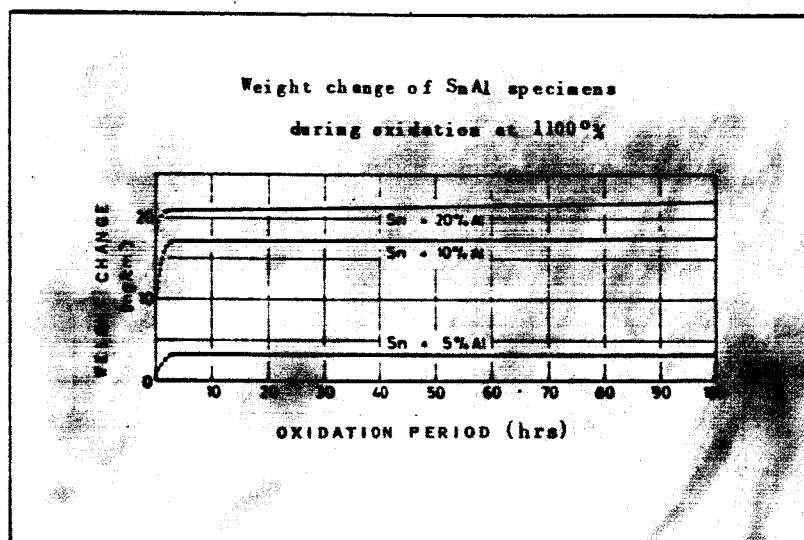


Fig.7

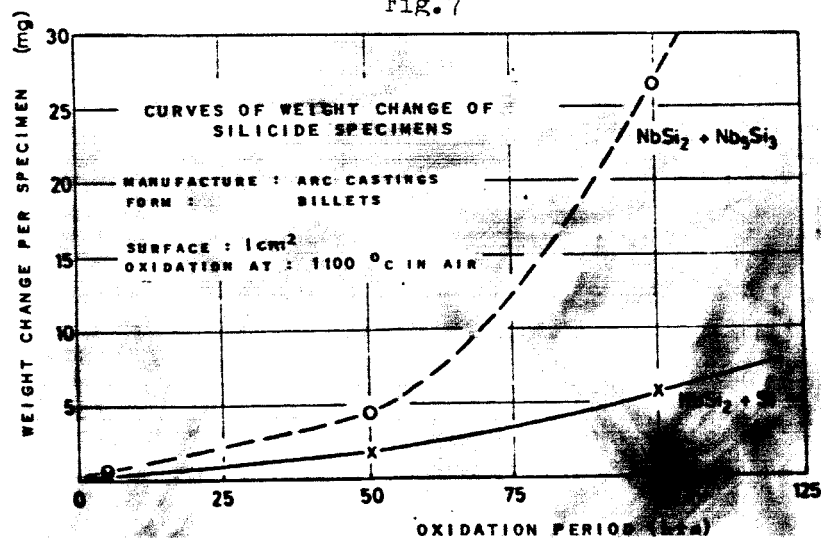


Fig.8

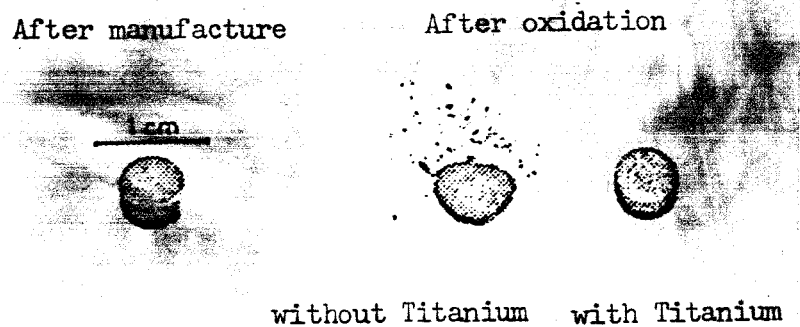


Fig.9 Phenomenon of "Pest"  
(NbSi<sub>2</sub> with and without titanium)

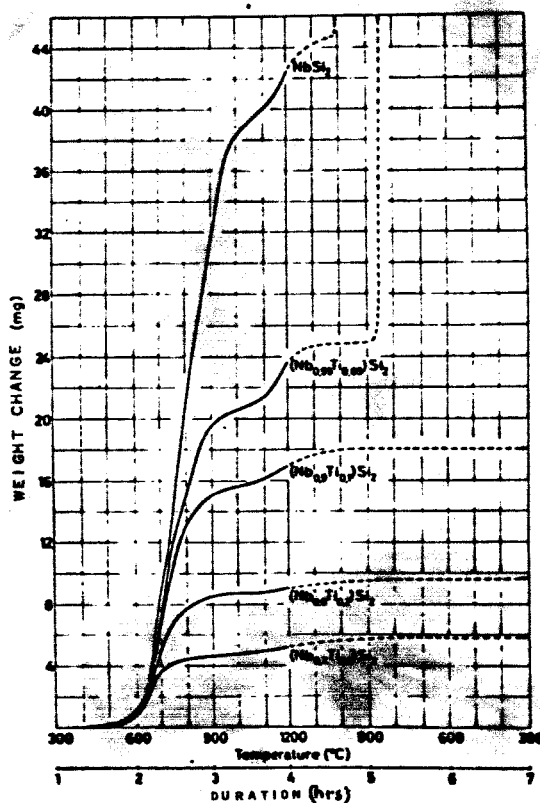


Fig.10 Weight Changes during Oxidation of Fritted NbSi<sub>2</sub>  
with Titanium (Phenomenon of Silicide Pest)

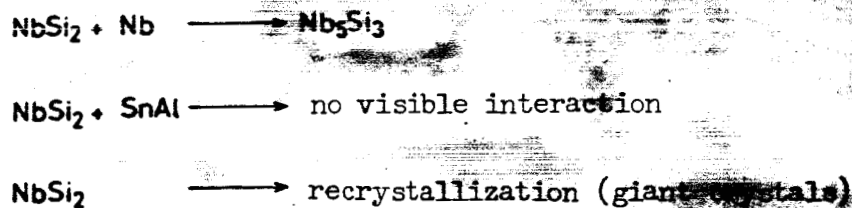


Fig.11 Modifications of the Layer by Diffusion

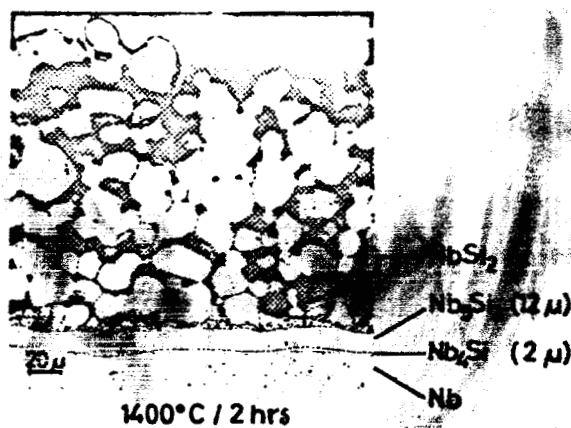


Fig.12 Reaction:  $\text{NbSi}_2 + \text{Nb} \rightarrow \text{Formation of Nb}_5\text{Si}_3 \text{ and Nb}_4\text{Si}$

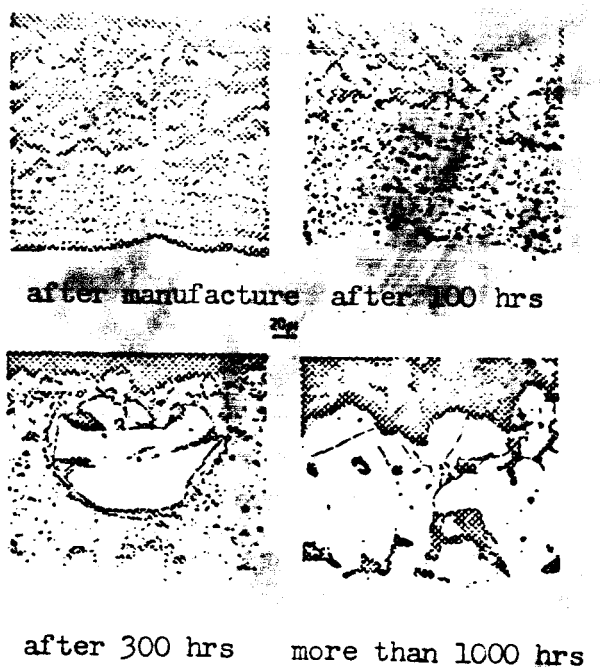


Fig.13 Recrystallization of NbSi<sub>2</sub> at 1100°C

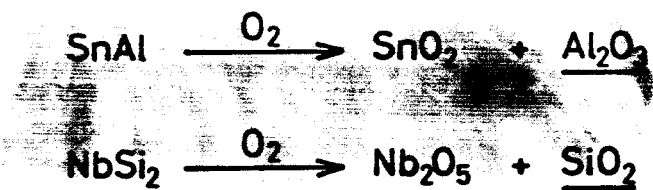


Fig.14 Depletion of the Coating by Oxidation

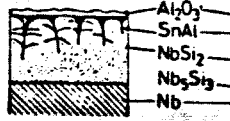
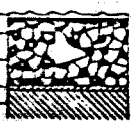
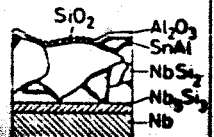
STATUS OF OXIDATION	AT BEGINNING	LATER	TOWARD END
			
PROTECTIVE LAYER		$Al_2O_3$	$SiO_2$ AT SPOTS WHERE $Al_2O_3$ IS DEPLETED
SENSITIVITY TO PEST	NOT SENSITIVE		SENSITIVE
STRUCTURE	SnAl FINELY DISPERSED	SnAl AGGLOMERATED PRIMARY RECRYSTALLIZATION OF $NbSi_2$	SnAl STRONGLY AGGLOMERATED SECONDARY RECRYSTALLIZATION OF $NbSi_2$

Fig.15 Structural Changes during Oxidation

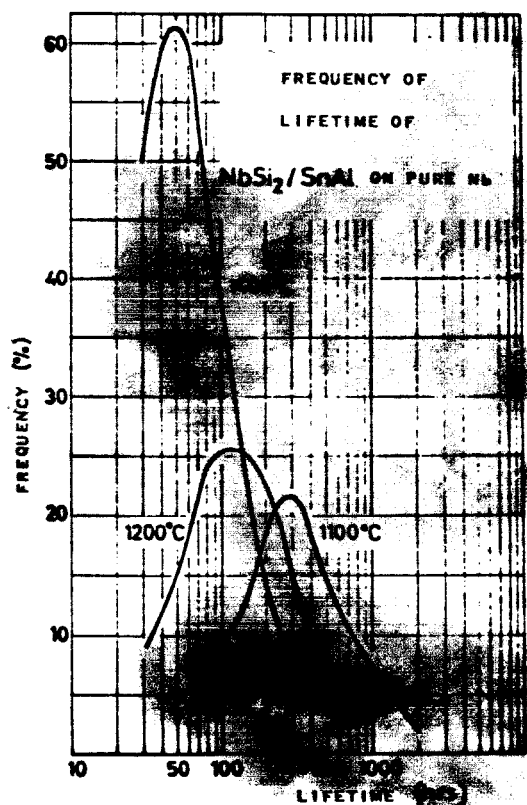


Fig.16

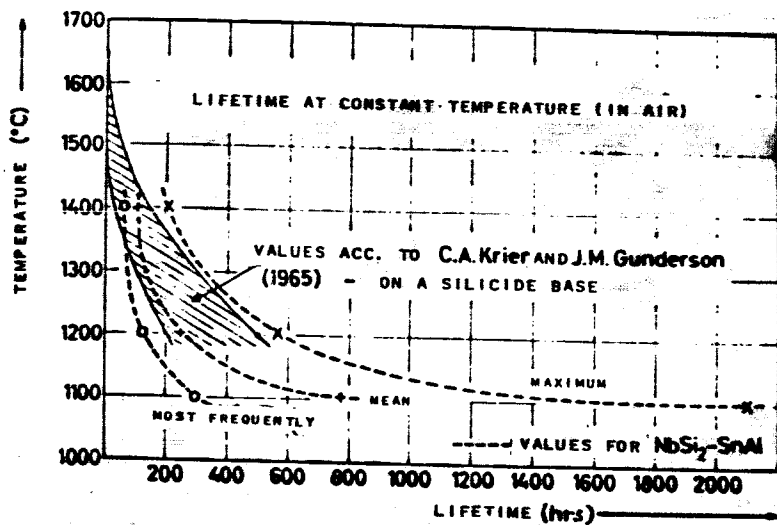
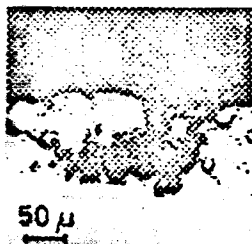
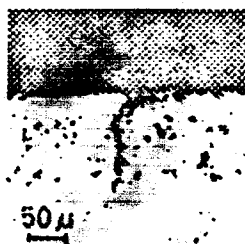


Fig.17

without Titanium

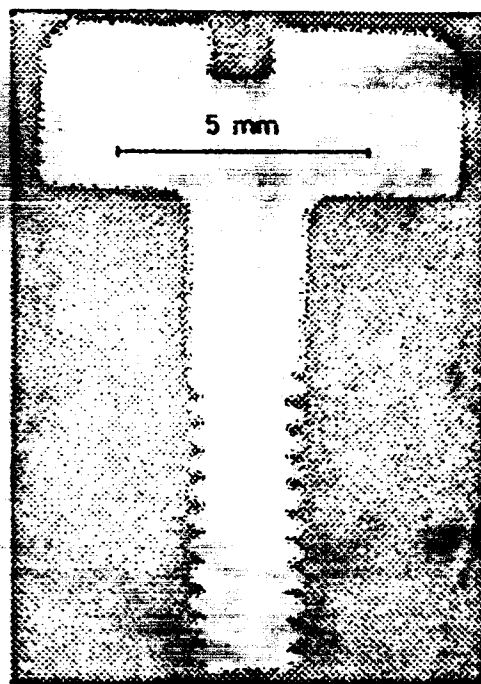


with Titanium



120 cycles of 30 min.: 150°C → 1200°C → 150°C

Fig.18 Cyclic Test



Appearance after 50 hrs at 1400 °C

Fig.19 Molybdenum Screw